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(12) UK Patent Application (19) GB (11) 2 044 258 A

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(21) Application No 8005722  
(22) Date of filing 20 Feb 1980

(30) Priority data

(31) CI 1916

(32) 21 Feb 1979

(33) Hungary (HU)

(43) Application published  
15 Oct 1980

(51) INT CL  
C07D 215/12  
A23K 3/00

(52) Domestic classification

C2C 1534 213 247 250

251 25Y 292 29Y 30Y 394

39Y 421 425 426 42Y 560

60Y 806 80Y AA QG

A2B 340 402 421 422 423

603 604 630 631 632 633

644 660 BCF

(56) Documents cited

None

(58) Field of search

C2C

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(54) **Quinoline derivatives useful as antioxidants, their preparation and compositions containing them**

(57) (2, 2 - Dimethyl - 1, 2 - dihydroquinolin - 4 - yl) - methyl - sulfonic acid and salts thereof are useful as antioxidants e.g. in animal feedstuffs. It may be made by sulfonation of 2, 2, 4 - trimethyl - 1, 2 - dihydroquinoline under mild conditions.

GB 2 044 258 A

## SPECIFICATION

## Quinoline derivatives useful as antioxidants, their preparation and compositions containing them

5 This invention relates to 2, 2 - dimethyl - 1, 2 - dihydroquinoline derivatives, to a process for the preparation thereof and to compositions containing them. More particularly, this invention relates to the  
 10 new (2, 2 - dimethyl - 1, 2 - dihydroquinolin - 4 - yl) - methylsulfonic acid and the salts thereof as well as to a process for the preparation of these compounds. (2, 2 - Dimethyl - 1, 2 - dihydroquinolin - 4 - yl) - methylsulfonic acid and the salts thereof have valuable  
 15 antioxidant properties and accordingly, can be used as antioxidants in various mixtures. The mixtures and the use of the new 2, 2 - dimethyl - 1, 2 - dihydroquinoline derivatives as antioxidants are also within the scope of the invention.

20 The feedstuffs used in huge quantities in animal husbandry always contain biologically active substances which are sensitive to oxidation. These substances are generally stabilized by antioxidants, which should be devoid of any injurious effect on the  
 25 animals at the effective concentration and should be eliminated rapidly, without leaving behind any residue.

It is well known that certain 1, 2 - dihydroquinoline derivatives have valuable antioxidant properties.

30 Preferred compounds of this type are for example disclosed in the Hungarian Patents Nos 149,469; 157,370; 161,563 and 162,358; in the South African patent 712,702 and in the Japanese patents 70,48-11.103.

35 The commercially available 1, 2 - dihydroquinoline antioxidants are dark coloured, non-uniform, viscous or amorphous substances. Due to their good solubility in lipids and poor water-solubility these compounds can be accumulated in the fatty tissues  
 40 of the animal organism and may cause the discolouration thereof.

The present invention provides a well-defined, uniform, water-soluble antioxidant which has a wide-ranging applicability.

45 (2, 2 - Dimethyl - 1, 2 - dihydroquinoline - 4 - yl) - methylsulfonic acid - hereinafter "sulfonic acid" - and the salts thereof can be prepared by sulfonating 2, 2, 4 - trimethyl - 1, 2 - dihydroquinoline under mild conditions, e.g. in an appropriately chosen reaction  
 50 medium, and if desired, converting chosen reaction medium, and if desired, converting the product obtained into a salt thereof.

The term "mild conditions" is used herein to define reaction conditions which ensure that the  
 55 undesired side reactions are avoided. When strong sulfonating agents, for instance oleum, are used, the dihydroquinoline molecule is sulfonated in the 7-position [W. H. Cliffe, J. Chem. Soc. 1933, p. 1327]. Sulfonation may be carried out in the temperature range of 20 to 80°C, preferably between 35°C and 45°C. Preferred sulfonating agents are sulfuric acid, chlorosulfonic acid, sulfur trioxide or a mixture of any of these.

The term "appropriately chosen reaction  
 60 medium" as used herein refers to organic solvents

which do not react with the sulfonating agents used. Preferably chlorinated hydrocarbons such as methylene chloride, carbontetrachloride; saturated hydrocarbons such as petrol; or saturated

65 heterocyclic compounds such as dioxane are used as a reaction medium.

The sulfonic acid obtained is preferably directly converted into a corresponding salt by using known basic reactants, preferably hydroxides, carbonates

70 or acetates of mono- and di-valent cations, such as ammonium, alkali metal and alkaline earth metal cations, e.g. sodium, potassium, magnesium and calcium ions or other metal ions, for example iron and zinc ions.

75 80 The salts are preferably isolated from the reaction mixture by pouring the mixture onto ice, followed by extraction with acetone and subsequent evaporation. The salts can be further purified by recrystallization. The products obtained can contain crystal

85 water, which can be eliminated by heating or for example by boiling with toluene. The free sulfonic acid can be recovered from a salt thereof preferably by using a cation exchange resin.

2, 2, 4 - Trimethyl - 1, 2 - dihydroquinoline used as

90 95 a starting material in the process according to the invention is for example disclosed in the Hungarian Patent 149,469. According to this patent said compound is prepared by reacting 1 mole of aniline with 2 moles of acetone in the presence of a suitable catalyst.

The valuable antioxidative properties of the sulfonic acid according to the invention are illustrated by the data listed in Table 1. The data set forth in Table 1 are the average results of numerous comparative tests. As a test material sunflower oil was

100 used, which was previously freed from natural antioxidants. The samples were kept in an uncovered round bottomed flask at 28°C. The peroxide number was determined by WEHLER's method, at intervals indicated in the table. From the results obtained it can be concluded that the antioxidant activity of the compounds according to the invention is superior to that of the compounds used for comparison.

110 In another test - carried out in numerous repetitions - the carotene-preserving activity of the compounds according to the invention was tested on lucerne meal in comparison with samples devoid of any antioxidant agent and with a commercially used antioxidant "BHI".

The change in the carotene content of lucerne meal was examined under natural conditions, at 26°C, under a relative humidity of 70%, in diffuse light. The results obtained are summarized in Table

120 115 2. The results clearly show that the new compounds according to the invention have a significant and excellent carotene-preserving activity.

The compounds according to the invention, due to their low toxicity, excellent antioxidant and favourable physical properties, e.g. microcrystalline structure, powdery state, good water-solubility, white colour, can advantageously be used in the pharmaceutical, cosmetic and food industry, or in the production of synthetic materials (e.g. resins) and rubber, which are the typical fields of application of

antioxidants. It is especially preferred to use them in fodder mixtures, nutriments and premixes.

The antioxidants are preferably introduced into the fodder mixtures as additives and/or as premixes.

5 In this way the oxygen-labile substances which are an essential component of a nutritionally balanced fodder ( $\beta$ -carotene, A-, E-, D-vitamins etc.) are stabilized from the outset. The stabilization is of primary importance when the premixes contain also trace elements which can act as oxidation catalysts.

10 In one aspect of the invention there are provided mixtures containing oxidation-sensitive substances, in which a compound according to the invention is present in an amount of 0.001 to 10% by weight. The use of these mixtures is also within the scope of the invention.

15 The compounds according to the invention are advantageously used in premixes, fodder additives, fodder mixtures and nutriments and ensure that these mixtures can be stored for a long time without any change in the easily oxidisable, biologically active substances contained therein.

20 The premixes and fodder additives contain the antioxidants according to the invention e.g. in the range of 100 to 100,000, preferably 0.01 to 10% by weight, depending on the field of application. It is preferred to form a homogenous mixture from the antioxidant and the oxidation-sensitive substance, which is then supplemented with the further components of the premix or fodder additive. The premixes contain for example dry seeds of fodder or various milling products as a carrier. The premixes are then admixed with other fodder components and converted into fodders ready of consumption.

25 Some typical fodder ingredients are cob meal, bran, soya meal, fish meal, beet sugar, wheat meal, lucerne meal, sunflower extract. As a fodder supplement dicalcium phosphate, fodder lime, fodder salt, fodder briquette can be used. Finally, various diluents, solvents, lubricants, carriers and other formulating agents can also be used in the fodder additives. By using the above listed ingredients the fodder additives can be formulated as powders, granules, powder mixtures, solutions, emulsions etc.

30 The nutriments and fodder mixtures contain 0.001 to 1% by weight of the antioxidants according to the invention.

35 The sulfonic acid salts according to the invention can be introduced into the nutriments or fodder mixtures not only in admixture with the premixes containing oxidation-sensitive substances, but also as so called "antioxidant premixes" or "antioxidant lipid mixtures". In this case the antioxidants are admixed with e.g. inert materials or lipid respectively, and the resulting antioxidant premixes or antioxidant lipid mixtures are added to the nutriments or fodder mixtures. The antioxidant lipid mixtures if desired, can contain also emulsifying agents.

40 The lipid mixtures can contain 0.01 to 2% by weight of the sulfonic acid or salt thereof.

45 An important advantage of the sulfonic acid and the salts thereof according to the invention over the known antioxidants consists in the fact that in a concentration of 0.001 to 1% by weight they show no

toxicity. They are well-defined, microcrystalline, white, powdery substances, with a good water-solubility, and can be incorporated into premixes, fodder additives, nutriments and fodder mixtures by conventional techniques.

50 The antioxidants according to the invention do not accumulate in the animal organism and are rapidly eliminated. For example, in poultry fed with nutriments which had been stabilized with the aforementioned sulfonic acid no harmful residue could be detected. Due to their fodder stabilizing activity, the present antioxidants promote the weight gain of the animals.

55 The antioxidants according to the invention can advantageously be combined with known, lipophilic antioxidants, especially when the substance liable to oxidation is also strongly lipophilic. A preferred combination is a 2:1 mixture of the sodium salt of the sulfonic acid according to the invention and the known Ethoxyquin (see Table 1) or thereabouts.

60 In four times its usual concentration, i.e. about 1000 ppm, the sodium salt of the sulfonic acid according to the invention has a strong activity in protecting sunflower oil from growing rancid (see Table 1). This fact is of particular interest primarily when prolonged storage is unavoidable. It is to be noted that the known antioxidants provide no further protection when used in concentrations exceeding the usual level.

65 Further details of the invention are to be found in the following examples which are for illustration only.

*Example 1*

70 To 40 ml of carbon tetrachloride 32 ml of concentrated sulfuric acid are added with stirring. The solution is cooled to 0°C and 17.3 g. (0.1 mole) of 2, 2, 4-trimethyl - 1, 2 - dihydroquinoline are added, whereupon it is kept at an internal temperature of 40°C. The two phases are separated. The lower phase is extracted with 40 ml of carbon tetrachloride and poured onto ice. Thereafter two 100-ml portions of a 5 N sodium hydroxide solution and 150 ml of a 10 N sodium hydroxide solution are added portionwise followed by the addition of water up to 650 ml. The alkaline solution is extracted with acetone. The acetone phase is evaporated *in vacuo* and the dark brown solution obtained is poured into ethyl acetate. The suspension obtained is stirred for 1 hour, filtered, washed with a mixture of ethyl acetate and methanol and dried under exclusion of direct illumination. 25.1 g. of (2, 2 - dimethyl - 1, 2 - dihydroxyquinolin - 4 - yl) - methylsulfonic acid sodium salt are obtained, melting at 66 to 68°C.

75 NMR spectrum: chemical shift: 6.66-7.5 5.9 4.1 1.33 intensity: 4 1 2 6 multiplicity: multiplett singulett

80 Analysis:  
Calculated: C=43.76 H=6.07 N=4.25 Na=6.99 O=29.17 S=9.72

85 Found: C=42.97 H=5.91 N=4.23 Na=7.00 O= - S=9.53

90 Water content (DSC): Calculated: 16.4% Found: 16%

*Example 2*

95 Into 40 ml of carbon tetrachloride 23.3 g (0.02 mole) of chlorosulfonic acid are added. To the solu-

tion 17.3 g (0.1 mole) of 2, 2, 4 - trimethyl - 1, 2 - dihydroquinoline are added at 0°C. It is then kept at 40°C for 4 hours and subsequently the procedure described in Example 1 is followed. 28.8 g (87.5%) of 5 (2, 2 - dimethyl - 1, 2 - dihydroquinolin - 4 - yl) - methylsulfonic acid sodium salt are obtained. The product has the same characteristics as the product of Example 1.

*Example 3*

- 10 Following the procedure described in Example 2 but neutralizing the acidic solution obtained after pouring the reaction mixture on ice, with a 5 N sodium hydroxide solution, making up the neutral mixture to 650 ml with a 35% aqueous calcium acetate solution and finally admixing the suspension obtained with 500 ml of acetone two phases are obtained. After separating the phases the acetone phase is worked up as described in Example 1 to yield 29.9 g of (2, 2 - dimethyl - 1, 2 - dihydroquinolin - 4 - yl) - methylsulfonic acid calcium salt, melting at 72 to 75°C. Yield: 86.6%.
- 15 Calcium content: Calculated: 11.3% Found: 11.1% Water content: Calculated: 15.6% Found: 15.3. (DSC)

*Example 4*

- 20 6.5 g. of (2, 2 - dimethyl - 1, 2 - dihydroquinolin - 4 - yl) - methylsulfonic acid sodium salt trihydrate in 20 ml. of water are passed through a chromatographic column filled with 120 g of DOWEX (Registered Trade Mark) 50 WX 10 cation exchange resin. The column is washed with distilled water and the eluted solution is evaporated. The precipitated substance is filtered, washed with ethyl acetate and dried at room temperature. 4.5 g. (88%) of (2, 2 - dimethyl - 1, 2 - dihydroquinolin - 4 - yl) - methylsulfonic acid are obtained, melting at 256 to 260°C.

*Example 5*

- To a solution of 13.2 g. of (2, 2 - dimethyl - 1, 2 - dihydroquinolin - 4 - yl) - methylsulfonic acid sodium salt in 10 ml of methanol 2.7 g of zinc chloride are added. The solution is stirred at room temperature of 2 hours, whereupon it is diluted with 40 ml of water. The solution is then evaporated *in vacuo* on water bath. 9.9 g (87%) of (2, 2 - dimethyl - 1, 2 - dihydroquinolin - 4 - yl) - methylsulfonic acid zinc salt are obtained, melting at 98 to 100°C.

*Example 6*

In a counterflow, three-stage quick mixer the following broiler premix is prepared:

50	vitamin A	1 100 000 IU
	vitamin D-3	220 000 IU
	vitamin E	1 500 IU
	vitamin K	250 mg
	vitamin B-1	200 mg
	vitamin B-2	600 mg
55	vitamin B-6	200 mg
	vitamin B-12	2 mg
	vitamin C	1 500 mg
	Ca-d-pantothenate	1 300 mg
	folic acid	30 mg
60	nicotinic acid	3 500 mg
	biotin	2 mg
	antioxidant according to Example 1	14 000 mg
	choline chloride	60 000 mg
65	clopidol (3, 5 - dichloro -	

2, 6 - dimethyl - 4 - pyridinol) 12 500 mg

Zn SO<sub>4</sub> x H<sub>2</sub>O in a quantity corresponding to 5200 mg of Zn<sup>2+</sup>

70 Ca(PO<sub>4</sub>)<sub>2</sub> x H<sub>2</sub>O in a quantity corresponding to 100 mg of iodine

CoSO<sub>4</sub> x 7H<sub>2</sub>O in a quantity corresponding to 15 mg of Co<sup>2+</sup>

MnO (amorphous) in a quantity corresponding to 6600 mg of Mn<sup>2+</sup>

CuSO<sub>4</sub> x 5H<sub>2</sub>O in a quantity corresponding to 500 mg of Cu<sup>2+</sup>

80 FeSO<sub>4</sub> x 7H<sub>2</sub>O in a quantity corresponding to 3000 mg of Fe<sup>2+</sup>

Na<sub>2</sub>SeO<sub>3</sub> in a quantity corresponding to 8 mg of Se carrier (wheat flour) ad 1000 g.

85 The premix is blended with 100 kg of a fodder mixture, optionally together with phosphorus- and calcium-containing fodder supplements, to form a homogenous mixture.

*Example 7*

90 In a three-stage, counterflow quick mixer the following premix is prepared for feeding egg-laying poultry:—

vitamin A 1 000 000 IU

vitamin D-3 200 000 IU

95 vitamin E 1 600 IU

vitamin K 200 mg

vitamin B-1 200 mg

vitamin B-2 500 mg

vitamin B-6 200 mg

100 vitamin B-12 2 mg

vitamin C 1 000 mg

Ca-d-pantothenate 1 300 mg

folic acid 30 mg

nicotinic acid 3 000 mg

105 a 2:1 mixture of the compound of Example 1 and Ethoxyquin 12 000 mg

cholin chloride 50 000 mg

DL-methionine 40 000 mg

110 ZnSO<sub>4</sub> x H<sub>2</sub>O in a quantity corresponding to 5200 mg of Zn<sup>2+</sup>

Ca(PO<sub>4</sub>)<sub>2</sub> in a quantity corresponding to 100 mg of iodine

115 CoSO<sub>4</sub> x 7H<sub>2</sub>O in a quantity corresponding to 15 mg of Co<sup>2+</sup>

MnO (amorphous) in a quantity corresponding to 6600 mg of Mn<sup>2+</sup>

120 CuSO<sub>4</sub> x 5H<sub>2</sub>O in a quantity corresponding to 500 mg of Cu<sup>2+</sup>

FeSO<sub>4</sub> x 7H<sub>2</sub>O in a quantity corresponding to 3000 mg of Fe<sup>2+</sup>

Na<sub>2</sub>SeO<sub>3</sub> in a quantity corresponding to 8 mg of Se

125 carrier (wheat flour) ad 1000 g

The premix is blended with 100 kg of fodder mixture, optionally together with phosphorus- and calcium-containing fodder supplements, to form a homogenous mixture.

**Example 8**

The following premix is prepared for feeding porkers:

5	vitamin A	1 000 000 IU		
5	vitamin D-3	140 000 IU	70	
	vitamin E	1 600 IU		
	vitamin K-3	160 mg		
	vitamin B-2	500 mg		
	vitamin B-6	200 mg		
10	vitamin B-12	2 mg	75	
	vitamin C	250 mg		
	Ca-d-pantothenate	1 200 mg		
	nicotinic acid	1 500 mg		
15	antioxidant of Example 1	1 500 mg	80	
	choline chloride	40 000 mg		
	zinc bacitracin	1 500 mg		
	L-lysine-HCl	40 000 mg		
20	ZnSO <sub>4</sub> x H <sub>2</sub> O	in a quantity corresponding to 9000 mg of Zn <sup>2+</sup>		
	Ca(IO <sub>3</sub> ) <sub>2</sub>	in a quantity corresponding to 100 mg of iodine	85	
	CoSO <sub>4</sub> x 7H <sub>2</sub> O	in a quantity corresponding to 3500 mg of Co <sup>2+</sup>		
25	CuSO <sub>4</sub> x 5H <sub>2</sub> O	in a quantity corresponding to 5000 mg of Cu <sup>2+</sup>	90	
	FeSO <sub>4</sub> x 7H <sub>2</sub> O	in a quantity corresponding to 12000 mg of Fe <sup>2+</sup>		

**30 Carrier (wheat flour) ad 1000 g**

The premix is homogenously blended with 100 kg of fodder mixture.

**Example 9**

35 In a two-stage "Nautor" epicyclic mixer the following premix is prepared for feeding dairy cattle:—

40	vitamin A	350 000 IU		
	vitamin D-3	300 000 IU		
	antioxidant of Example 3	1 000 mg		
	MgO	in a quantity corresponding to 150 000 mg of Mg <sup>2+</sup>		
45	ZnSO <sub>4</sub> x H <sub>2</sub> O	in a quantity corresponding to 14 000 mg of Zn <sup>2+</sup>	110	
	Ca(IO <sub>3</sub> ) <sub>2</sub>	in a quantity corresponding to 500 mg of iodine		
	MnO (amorphous)	in a quantity corresponding to 9 000 mg of Mn <sup>2+</sup>		
50	CoSO <sub>4</sub> x 7H <sub>2</sub> O	in a quantity corresponding to 600 mg of Co <sup>2+</sup>	115	
	CuSO <sub>4</sub> x 5H <sub>2</sub> O	in a quantity corresponding to 2500 mg of Cu <sup>2+</sup>		
55	FeSO <sub>4</sub> x 7H <sub>2</sub> O	in a quantity corresponding to 30 000 mg of Fe <sup>2+</sup>		
	carrier (wheat flour) ad 1 000 g			

60 The premix is homogenously blended with 100 kg of fodder, optionally together with phosphorus- and calcium-containing supplements.

**Example 10**

On the basis of the broiler premix obtained in Example 6 the following broiler nutriment is prepared:

cob meal	56.3%
wheat meal	10.0%
soy meal (47%, extracted)	22.0%
fish meal (70%)	8.0%
dicalcium phosphate	1.3%
fodder lime	1.0%
fodder salt	0.4%
broiler premix	1.0%

**Example 11**

On the basis of the premix obtained in Example 7 the following nutriment is prepared:

cob meal	54.5%
wheat meal	10.0%
fish meal (70%)	1.0%
soy meal (47%)	16.5%
extracted sunflower	3.5%
lucerne meal	5.0%
dicalcium phosphate	1.6%
fodder briquette	6.5%
fodder salt	0.4%
premix (Example 7)	1.0%

100.0%

**Example 12**

95 0.5 parts by weight of the antioxidant prepared in Example 1 are admixed with soy lecithin (50%), whereupon 97 parts by weight of fat are added and the ingredients are admixed homogenously. On the basis of the antioxidant-fat mixture obtained, a rat nutriment described in Example 13 is prepared.

**Example 13**

On the basis of the antioxidant-fat mixture obtained in Example 12 the following rat nutriment is prepared:

fish meal (70% crude protein)	13.0%
soy meal (extracted, 47% protein)	34.0%
antioxidant-fat mixture of Example 12	4.0%
cob meal	26.0%
bran	8.0%
beet sugar	10.0%
mineral materials	3.0%
premix	2.0%

100.0%

**Example 14**

120 25 g of the antioxidant obtained in Example 1 are homogenously admixed with 975 g of limestone dust and the premix obtained is incorporated into fodder mixtures in a quantity of 1%.

**Example 15**

125 16 g of the antioxidant obtained in Example 1 are admixed with 9 g of Ethoxyquin adsorbed on 4 g of silica. The premix obtained is incorporated into fodder mixtures in a quantity of 0.5%.

Table 1  
Protection of sunflower oil from rancidity

Days	peroxide number						
	without antioxidant	250 ppm of XAX	250 ppm of Ethoxyquin	250 ppm of BHT	250 ppm of the antioxidant of Example 1	250 ppm of a 2:1 mixture of the antioxidant of Example 1	1000 ppm of the antioxidant of Example 1 and Ethoxyquin
1	2	1	1	1	1	1	0
2	12	9	8	8	7	6	2
7	24	20	17	18	15	13	5
12	55	45	39	37	35	33	11
15	90	68	58	55	54	55	16
18	139	96	81	76	72	76	19

XAX = 2-methylene-bis-(2,2,4-trimethyl-1,2-dihydroquinoline)

Ethoxyquin = 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline

BHT = 2,6-di-tert-butyl-4-methylphenol

Table 2  
Change in the carotene concentration of lucerne meal

Days	Carotene mg/kg		
	without antioxidant	250 ppm of BHT	250 ppm of the antioxidant of Example 1
1	135	137	138
7	114	124	131
28	80	98	112
49	57	71	92
70	34	46	84

#### CLAIMS

1. (2,2-Dimethyl-1,2-dihydroquinolin-4-yl)-methylsulfonic acid and the salts thereof.
2. Alkali metal and alkaline earth metal salts of (2,2-dimethyl-1,2-dihydroquinolin-4-yl)-methylsulfonic acid.
3. Sodium, ammonium, calcium and zinc salts of (2,2-dimethyl-1,2-dihydroquinolin-4-yl)-methylsulfonic acid.
4. A process for the preparation of (2,2-dimethyl-1,2-dihydroquinolin-4-yl)-methylsulfonic acid and the salts thereof which comprises reacting 2,2,4-trimethyl-1,2-dihydroquinolin with a sulfonating agent under mild conditions and if desired, converting the sulfonic acid obtained into a salt thereof.
5. A process as claimed in claim 4 which includes preparing a salt of said sulfonic acid formed with a mono- or divalent cation.
6. A process as claimed in claims 4 or 5 wherein sulfuric acid, chlorosulfonic acid, sulfur trioxide or a
7. A process as claimed in any one of claims 4 to 6 wherein the sulfonation is performed at a temperature of 20 to 80°C.
8. A process as claimed in claim 7 wherein said temperature is 35 to 45°C.
9. A process as claimed in any one of claims 4 to 8 wherein the reaction is performed in an organic solvent.
10. A process as claimed in claim 9 wherein said organic solvent comprises a saturated or chlorinated hydrocarbon or a heterocyclic solvent.
11. A process as claimed in any one of claims 4 to 10 wherein the sulfonic acid obtained is converted into a salt thereof without isolation.
12. A process as claimed in claim 4, substantially as described herein.
13. A process as claimed in claim 4, substantially as described herein with reference to any one of Examples 1 to 3.
14. A stabilised composition comprising one or

more oxidation-sensitive substances and 0.001 to 10% by weight of at least one compound of claims 1 to 3.

15. A composition as claimed in claim 14 including 0.001 to 10% by weight of a further antioxidant.

16. A composition as claimed in claim 15 wherein said further antioxidant comprises 6 - ethoxy - 2, 2, 4 - trimethyl - 1, 2 - dihydroquinoline.

17. A composition as claimed in claim 16 comprising about 2 parts by weight of sodium (2, 2 - dimethyl - 1, 2 - dihydroquinolin - 4 - yl) - methylsulfonate and about one part by weight of 6 - ethoxy - 2, 2, 4 - trimethyl - 1, 2 - dihydroquinoline.

18. A composition as claimed in any of claims 14  
15 to 17 which is a fodder or nutrient comprising  
0.001 to 1% by weight of a compound of claims 1 to  
3, and optionally a physiologically acceptable prop-  
ortion of said further antioxidant.

19. A composition as claimed in any of claims 14  
20 to 17 which is a cosmetic, pharmaceutical, synthetic  
resin or rubber composition.

20. A composition as claimed in claim 14, substantially as illustrated in any one of Examples 6 to 11 or 13 to 15.

25 21. An antioxidant composition comprising 0.01 to 10% by weight of at least one compound of claims 1 to 3 and a carrier.

22. A composition as claimed in claim 21 in the form of a fodder premix.

30 23. A composition as claimed in claim 21  
wherein said carrier comprises a lipid material  
and/or an emulsifying agent, said composition com-  
prising 0.01 to 2% by weight of said at least one  
compound of claims 1 to 3.

35 24. A composition as claimed in any of claims 21 to 23 including a further antioxidant.

25. A composition as claimed in claim 24 wherein said further antioxidant comprises 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline.

40 26. A composition as claimed in claim 21, substantially as illustrated in any one of Examples 12, 14 or 15.

27. The use of (2, 2 - dimethyl - 1, 2 - dihydro-quinolin - 4 - yl) - methylsulfonic acid and/or a salt thereof as an antioxidant in mixtures containing oxidation-sensitive substances.

Printed for Her Majesty's Stationery Office by The Tweeddale Press Ltd.,  
Berwick-upon-Tweed, 1980.  
Published at the Patent Office, 25 Southampton Buildings, London, WC2A 1AY,  
from which copies may be obtained.

